THE GROUND STATE ENERGY OF HEAVY ATOMS (Tosio Kato Centennial Conference)

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THE GROUND STATE ENERGY OF HEAVY ATOMS

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ABSTRACT. We review results on the asymptotic behavior of the groundstate energy and the reduced one-particle ground state density of large atoms.

1. MODELS OF AN ATOM

We will review the description of large atoms, in particular the asymptotic behavior of the ground state energy and the ground state density. This can be done in the context of various models which – heuristically – should describe the atom – when compared with experimental values of these quantities – to increasing order of correctness. Some of those models for N electrons are discussed here. For simplicity we will focus on the one center case, i.e., the external field is generated by a nucleus of charge Z although some of the results are also true for molecules. Moreover, we will concentrate on the most prominent case, namely neutral atoms, i.e., $N = Z$.

Thomas-Fermi: The Thomas-Fermi energy $E_{\mathrm{TF}}(N,Z)$ of N electrons in the field of a nucleus of charge Z is the infimum of the Thomas-Fermi functional (Lenz [37])

$$\mathcal{E}_{\mathrm{TF}}(\rho) := \int_{\mathbb{R}^3} \left(\frac{3}{10} \left(3\pi^2\right)^{2/3} \rho(x)^{5/3} - \frac{Z}{|x|} \right) \mathrm{d}x + D[\rho]$$

where

$$D[\rho] := \frac{1}{2} \int_{\mathbb{R}^3} \mathrm{d}x \int_{\mathbb{R}^3} \mathrm{d}y \frac{\rho(x)\rho(y)}{|x-y|}$$

and ρ is taken over all $\rho \geq 0$ in $L^{5/3}(\mathbb{R}^3)$ with $\int_{\mathbb{R}^3} \mathrm{d}x \rho(x) \leq N$. Lieb and Simon [38] analyzed the functional mathematically and showed among other facts the existence and uniqueness of a minimizer. From the physical point Gombas [24] offers a classical review.

Schrödinger: The Schrödinger energy is the lowest spectral point $E_S(N,Z) := \inf \sigma(S_{N,Z})$ of the Schrödinger operator

$$S_{N,Z} = \sum_{n=1}^{N} \left(T_n - \frac{Z}{|x_n|} \right) + \sum_{1 \leq m < n \leq N} \frac{1}{|x_m - x_n|}$$

defined by the associated quadratic form on the anti-symmetric Schwartz functions $\bigwedge_{n=1}^{N} \mathfrak{h}$ with $\mathfrak{h} := \mathcal{S}(\mathbb{R}^3 : \mathbb{C}^2)$ (Friedrichs extension). Here $T := p^2/2$ with $p := -\mathrm{i}\nabla$.

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Chandrasekhar: The Chandrasekhar operator $C_{N,Z,c}$ is motivated by the naive quantization of the classical relativistic Hamiltonian. It can be defined as the Schrödinger operator $S_{N,Z}$ but with the operator of kinetic energy $T := \sqrt{c^2p^2 + c^4} - c^2$. The additional parameter c is – in physical terms – known as the velocity of light. The Chandrasekhar energy $E_C(N, Z)$ is the lowest spectral point of $C_{N,Z,c}$.

Of course this is only meaningful, if and only if $Z/c \leq 2/\pi$, the necessary and sufficient condition for the form being bounded from below (Kato [35, p. 307], see also Herbst [29] and Chen and Siedentop [7]).

Brown-Ravenhall: The no-pair operator $B_{N,Z,c}$ in the free picture (Sucher [59]), also called Brown-Ravenhall operator (Brown and Ravenhall [6], see also Bethe and Salpeter [5]), can again be defined similarly to Schrödinger operator $S_{N,Z}$, however, with

$$T := D_{0,c} := c\boldsymbol{\alpha} \cdot p + \beta c^2 - c^2$$

and one-particle states in $\mathfrak{h} = \chi_{\mathbb{R}_+}(D_{0,c})(\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^4))$ which intuitively is interpreted as the orthogonal space of the Dirac sea – here of the free Dirac operator $D_{0,c}$ – which is not accessible to electrons, i.e., poetically speaking the electrons are the vapor over the free Dirac sea. The Brown-Ravenhall energy $E_B(N, Z)$ is the lowest spectral point of $B_{N,Z,c}$.

Again, as in the Chandrasekhar case, this requires a restriction of the allowed coupling constant. For boundedness from below $Z/c \leq 2/(2/\pi + \pi/2)$ is necessary and sufficient (Evans et al [10], see also Tix [61, 62]).

Furry & Oppenheimer: The no-pair operator $F_{N,Z,c}$ in the Furry picture [59], for short the Furry operator, is defined as the Brown-Ravenhall operator, however, with one particle states $\mathfrak{h} = \Lambda_{Z,c}(\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^4))$ where $\Lambda_{Z,c}$ is the spectral projection of the Coulomb Dirac operator

$$D_{Z,c} := c\boldsymbol{\alpha} \cdot \tfrac{1}{\mathrm{i}}\nabla + c^2(\beta - 1) - \frac{Z}{|x|}$$

to the positive spectral subspace, i.e., $\Lambda_{Z,c} := \chi_{(0,\infty)}(D_{Z,c})$. In other words, the Furry electrons are the vapor over the Dirac sea defined as the negative spectral subspace of the one-particle Dirac operator with external potential. – Again there is a natural restriction on the coupling constant, namely $Z/c < 1$.

2. Some Classical Results

2.1. **Non-Relativistic Hamiltonian.** The classical Hamiltonian was introduced by Schrödinger [45, 46, 44] and solved for $N = 1$. But motivation for taking anti-symmetric states predates these works and goes back to Pauli [33]. However, it was Kato [34] (see also Kato [35]) who showed that $S_{N,Z}$ can be self-adjointly realized in $\bigwedge_{n=1}^{N} L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$ and can be viewed as perturbation of the Laplacian.

Shortly after Schrödinger's work it became clear that the hope for an analytical solution of the N-electron problem in quantum mechanics is at least as unrealistic as in classical mechanics. Driven by this insight, Thomas [60] and Fermi [20, 21] saw the necessity of an approximation which describes N electron systems in a simple way; they derived – on a physical level – the Thomas-Fermi theory with the intention to describe the energy and density roughly correct when many particles are involved and the external potential does not change much, i.e., in a certain

sense, the potential would commute locally with the momentum operator. The expectation was that $E_S(Z) \approx E_{TF}(Z)$. In fact Lieb and Simon [38] showed in their seminal paper published fifty years after Thomas and Fermi that indeed

$$E_S(Z) = E_{TF}(Z) + o(Z^{7/3}).$$

(Note that we find it convenient to formulate our results for the neutral case only, i.e., $N = Z$. In this case – when no confusion is possible – we tend to drop the index N. Note also that the Thomas-Fermi energy has the simple scaling relation $E_{TF}(Z) = E_{TF}(1)Z^{7/3}$.)

Based on the local commutativity assumption it was clear that a correction of the TF-model should come from the electrons close to the attractive singularity. In fact Scott [48] conjectured on this basis the following formula

$$E_S(Z) = E_{TF}(Z) + \frac{1}{2}Z^2 + o(Z^2)$$

which – was proven another ten years later (Siedentop and Weikard [54, 49, 50, 51, 52] (upper and lower bound) and Hughes [30, 31] (lower bound). The formula has been physically rederived, mathematically reproven and extended by various methods (Bach [1, 2], Ivrii and Sigal [32], Solovej and Spitzer [56], [4]). In fact Fefferman and Seco [16, 17, 18, 11, 19, 14, 12, 13, 15] obtained a three terms asymptotics.

2.2. **Relativistic Hamiltonians.**

2.3. **The Chandrasekhar Energy.** Since states at large distances from the nucleus have – at least intuitively – small kinetic energy, a non-relativistic description should still be appropriate for those states. However, at small distance the electrons are moving much faster. Thus, using a non-relativistic model for large Z atoms is physically inappropriate. Although mathematically possible as mentioned above, it cannot be expected to give physically relevant results. Instead a relativistic description is required. It should influence the electrons close to the nucleus strongly and thus contribute to the Scott correction. Since the relativistic energy is much weaker for large momenta, a lowering of the Scott term should occur. This was predicted by Schwinger [47] based on a heuristic modification of Scott's original observation. In fact, for large Z and $\gamma = Z/c$ fixed and less or equal $2/\pi$ one obtains for the Chandrasekhar ground state

$$E_C(Z) = E_{TF}(Z) + (\frac{1}{2} - s_C(\gamma))Z^2 + o(Z^2) \tag{1}$$

where $s_C(Z/c)$ is the sum of the difference of the negative eigenvalues of the operators $p^2/2 - \gamma/|x|$ and $(p^2+1)^{1/2} - 1 - \gamma/|x|$, i.e.,

$$s_C(\gamma) = \mathrm{tr}((S_{1,\gamma})_- - (C_{1,\gamma,1})_-). \tag{2}$$

This result is due to Solovej, Sørensen, and Spitzer [55] and Frank, Siedentop, and Warzel [22].

Note, that this model can be considered as a mathematical warm-up only, since its eigenvalues are – even in the one-particle case – too low compared with the one-particle Dirac eigenvalues. Moreover, it does not even cover the all known elements for the physical values of c and Z.

2.4. **The Energy of the Brown-Ravenhall Operator.** The above general consideration on fast moving inner electrons applies to all relativistic operators, i.e., also for the Brown-Ravenhall operator a lowering of the Scott term is expected. In fact on gets

$$E_B(Z) = E_{\mathrm{TF}}(Z) + (\frac{1}{2} - s_B(\gamma))Z^2 + o(Z^2) \tag{3}$$

where, analogously to the Chandrasekhar case,

$$s_B(\gamma) = \mathrm{tr}((S_{1,\gamma})_- - (B_{1,\gamma,1})_-) \tag{4}$$

with γ is fixed in $[0, (\pi/2 + 2/\pi)/2]$ (Frank, Siedentop, and Warzel [23]).

Although the eigenvalues of the one-particle Coulomb Brown-Ravenhall operator majorize the eigenvalues of the Coulomb Chandrasekhar operator and although it covers all known elements for the physical value of c the one-particle eigenvalues are still too low compared to the Dirac eigenvalues.

2.5. **The Energy of the Furry Operator.** The Furry operator is expected to yield the right asymptotic behavior of the ground state energy. Therefore we indicate the strategy of the proof in this case.

First we note that the hydrogenic Dirac operator $D_{Z,c}$ can be defined in a natural way with form domain $H^{1/2}(\mathbb{R}^3 : \mathbb{C}^3)$ when $Z/c < 1$ (Nenciu [42]). Furthermore, it is obvious that

$$D_{N,Z,c} := \sum_{n=1}^{N} D_{Z,c_n} + \sum_{1 \leq m < n \leq N} \frac{1}{|x_m - x_n|}$$

defined on all 4^N-spinors in the Schwartz space is a symmetric operator with corresponding form

$$\mathcal{E}[\psi] := (\psi, D_{N,Z,c}\psi). \tag{5}$$

However, we will admit only normalized anti-symmetric spinors because of the Pauli principle and require $\otimes_{n=1}^{N} \Lambda_{Z,c}\psi = \psi$ implementing the Dirac sea. Note that $\mathcal{E}$ is bounded from below on those functions. Obviously, $\mathcal{E}[\psi] \geq -c^2 N \|\psi\|^2$. This allows to define the Furry operator $F_{N,Z,c}$ as the self-adjoint operator associated with the form $\mathcal{E}$ restricted to those spinors.

For $\gamma \in (0,1)$ we define

$$\lambda_n^{\mathrm{S,H}} \text{ :n-th eigenvalue of } \left(p^2 - \frac{\gamma}{|x|}\right) \otimes 1_{\mathbb{C}^2} \tag{6}$$

$$\lambda_n^{\mathrm{D,H}} \text{ :n-th eigenvalue of } \boldsymbol{\alpha} \cdot p + \beta - 1 - \frac{\gamma}{|x|} \tag{7}$$

This allows to define the relativistic correction of the Scott term:

$$s_F(\gamma) := \frac{1}{\gamma^2} \sum_{n=1}^{\infty} (\lambda_n^{\mathrm{S,H}} - \lambda_n^{D,H}) \tag{8}$$

for $\gamma \in (0,1)$. Note that not only the non-relativistic eigenvalues but also the relativistic eigenvalues are explicitly known (Schrödinger [45], Gordon [25], Darwin [8]). In fact those energy levels were known before the Schrödinger equation and the Dirac equation (Balmer [3] and Sommerfeld [57]).

Since the Coulomb eigenvalues are ordered as follows: Schrödinger (including spin) bigger than Dirac bigger than Brown-Ravenhall bigger than Chandrasekhar (including spin) eigenvalues, one has

$$0 < s_F(\gamma) < s_B(\gamma) < s_c(\gamma).$$

This is a consequence of the variational principle for eigenvalues in gaps (see Griesemer et al. [27, 26], Morozov and Müller [40] and Müller [41]).

2.5.1. *Main Result.* We can now formulate the main result.

Theorem 1 (Handrek and Siedentop [28]). *There exists a constant $C > 0$ such that for all $Z > 0$ and $\gamma = \frac{Z}{c} \leq d < 1$ for some d one has*

$$\left| E_F(Z) - \left[E_{\mathrm{TF}}(Z) + \left(\frac{1}{2} - s_F(\gamma) \right) Z^2 \right] \right| \leq C Z^{47/24}. \tag{9}$$

Put differently: Fix $\gamma \in (0,1)$. As $Z \to \infty$

$$E_F(Z) = E_{\mathrm{TF}}(Z) + \left(\tfrac{1}{2} - s^D(\gamma) \right) Z^2 + o(Z^2) \tag{10}$$

uniformly in $\gamma = \frac{Z}{c} \leq d < 1$.

We indicate the strategy of proof here. The main point is that we do not control the relativistic energy directly but only relatively to the non-relativistic energy. Physically speaking we renormalize the energy. We outline this procedure for the lower bound. The upper bounds is – in spirit – similar.

2.5.2. *The Energy Shift from Hydrogenic Schrödinger to Hydrogenic Dirac Energies.* Using the explicit formulae for the eigenvalues one proves the following lemma:

Lemma 1. *Assume $\gamma_0 < 1$. Then there exists a constant $C \in \mathbb{R}$ such that for all $l \in \mathbb{N}$, $j = l \pm 1/2$, $j \geq 1/2$, and $\gamma \in [0, \gamma_0)$*

$$\left| \lambda^{\mathrm{D,H}}_{\gamma,n,l,j} - \lambda^{S,H}_{\gamma,n,l} + \frac{\gamma^4}{2\,(n+l)^3} \left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4} \frac{1}{n+l} \right) \right| \leq C\gamma^6 \frac{n}{(n+l)^4 l}. \tag{11}$$

This has the two important consequences:

Corollary 1. *Under the above assumptions*

$$0 \leq \lambda^{\mathrm{S,H}}_{\gamma,n,l} - \lambda^{\mathrm{D,H}}_{\gamma,n,l,j} \leq \frac{C\gamma^4}{(n+l)^3\, l}. \tag{12}$$

and

Corollary 2. *For $\gamma < 1$ the energy shift $s_F(\gamma)$ exists and is positive.*

2.5.3. *The Shift from Screened Schrödinger to Screened Dirac.* In the next step, one needs to control the error when replacing screened Dirac eigenvalues by Schrödinger eigenvalues for large angular momenta:

Lemma 2.

$$\sum_{l, 0 \leq j = l \pm \frac{1}{2}, n} \left(\lambda^{\mathrm{S,TF}}_{n,l,j} - \lambda^{\mathrm{D,TF}}_{n,l,j} \right) = O\left(\frac{\gamma^2 Z^2}{l^2} \right)$$

2.5.4. *Correlation Inequality.* An important step is the reduction to a one-particle problem. This is accomplished by using the correlation inequality of Mancas et al [39]

$$\sum_{1\leq\nu<\mu\leq N}\frac{1}{|\mathbf{x}_\nu-\mathbf{x}_\mu|}\geq\sum_{\nu=1}^{N}\left(\rho_Z^{\mathrm{TF}}*|\cdot|^{-1}(x_\nu)-\chi(\mathbf{x}_\nu)\right)-D[\rho_Z^{\mathrm{TF}}]. \tag{13}$$

where

$$\chi(\mathbf{x})=\int_{|\mathbf{x}-\mathbf{y}|<R_Z(\mathbf{x})}\frac{\rho_Z^{\mathrm{TF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\mathrm{d}\mathbf{y} \tag{14}$$

$R_Z(x)$ radius of the exchange hole defined by

$$\int_{|\mathbf{x}-\mathbf{y}|\leq R_Z(\mathbf{x})}\rho_Z^{\mathrm{TF}}(\mathbf{y})\mathrm{d}\mathbf{y}=\frac{1}{2}. \tag{15}$$

This gives a lower bound on the total Furry energy in terms of one- and zero-particle operators

Corollary 3 (Lower Bound on Furry).

$$\mathcal{E}[\psi]\geq\sum_{\nu=1}^{N}(\psi,(D_{0\nu}-1-\varphi_{\mathrm{TF}}(x_\nu)\psi))-D[\rho_Z^{\mathrm{TF}}]-\mathrm{C}Z^{5/3}$$

Now, we use the following consequece of the upper and lower bounds of Siedentop and Weikard [49, 52], see also [53]:

Theorem 2. *Pick* $L=[Z^{1/9}]$. *Then*

$$E_S(Z)=\sum_{n,l\leq L-1,0\leq j=l\pm\frac{1}{2}}\lambda_{n,l,j}^{\mathrm{S,H}}+\sum_{n,L\leq l,0\leq j=l\pm\frac{1}{2}}\lambda_{n,l,j}^{\mathrm{TF}}-D[\rho_Z^{\mathrm{TF}}]+\mathrm{C}Z^{47/24}$$

Armed with this result, we get the following lower bound on the shift of the total energy

$$E_S(Z)-E_F(Z) \tag{16}$$

$$\geq\sum_{l=0}^{L-1}\sum_{0\leq j=l\pm\frac{1}{2},n}\left(\lambda_{n,l,j}^{\mathrm{S,H}}-\lambda_{n,l,j}^{\mathrm{D,H}}\right) \tag{17}$$

$$-\sum_{l=L}^{\infty}\sum_{0\leq j=l\pm\frac{1}{2},n}\left(\lambda_{n,l,j}^{\mathrm{S,TF}}-\lambda_{n,l,j}^{\mathrm{D,TF}}\right)-\mathrm{C}Z^{47/48} \tag{18}$$

$$\geq s^D(\gamma)Z^2-\mathrm{C}Z^{47/48}. \tag{19}$$

This finishes the outline of the proof.

2.6. **Comparison with Experiment.** As already mentioned, one cannot expect that the Chandrasekhar and Brown-Ravenhall operators give quantitatively correct result for heavy atoms. However, the Furry picture gives numerical values up to chemical accuracy (Reiher and Wolf [43]).

If one is emboldened by this fact and dares to apply Stell's *Principle of Unreasonable Utility of Asymptotic Expansions* (G. Stell [58]) one gets the following graph.

- red diamonds, crosses: $(E_{\text{experimental}}(Z) - E_{\text{TF}}(Z))Z^{-2}$
- red solid: Schwinger's approximation
- blue: $\frac{1}{2} - s^D(Z/137)$

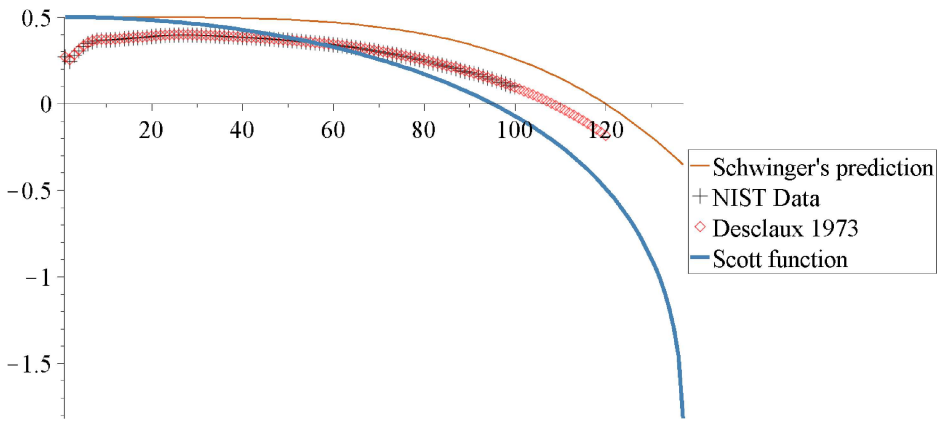

FIGURE 1. Comparison (see [28]) of the relativistic Scott function with data taken from the NIST database [36], Dirac-Fock calculations (Desclaux [9]), and Schwinger's original prediction (Schwinger [47]) plotted over Z for $c = 137$.

3. The Ground State Density

Energetic control yields also convergence of the ground state. Using a linear response argument Lieb and Simon[38] show

Theorem 3. *Assume ψ^S to be a groundstate of $S_{Z,Z}$; write $\tilde{\rho}_{\psi^S}$ for the associated one-particle groundstate density and ρ_{TF} the minimizer of the Thomas-Fermi functional with $Z = 1$. Moreover, let B be any measurable bounded subset of $\mathbb{R}^3$. Then the rescaled density ρ^S defined by*

$$\rho^S(x) := Z^{-2}\tilde{\rho}_{\psi^S}(Z^{-1/3}x)$$

converges to the Thomas-Fermi density in the following sense:

$$\boxed{\lim_{Z\to\infty}\int_B \mathrm{d}x\rho(x) = \int_B \mathrm{d}x\rho_{\text{TF}}(x).}$$

Fefferman and Seco [17] observed that the missing term in the correlation inequality yields automatically the convergence in Coulomb norm

Theorem 4. *As $Z \to \infty$*

$$D[\rho^S - \rho_{\text{TF}}] = O(Z^{-1/3}).$$

Corresponding considerations can be also carried through for the Chandrasekhar and Brown-Ravenhall operator (Merz [in preparation] and Merz and Siedentop [in preparation]). In particular one obtains in the Brown-Ravenhall case the following result:

Theorem 5. *Let ψ^B be a groundstate of $B_{Z,Z,c}$, let ρ^B be the rescaled groundstate density (as above) and fix $Z/c < 2/(2/\pi + \pi/2)$. Then, as $Z \to \infty$*

$$D[\rho^B - \rho_{\mathrm{TF}}] = O(Z^{-1/48}).$$

References

[1] Volker Bach. Ein Beweis der Scottschen Vermutung für Ionen. Master's thesis, Institut für Mathematische Physik, Technische Universität Braunschweig, Braunschweig, June 1989.

[2] Volker Bach. Ionization energies of bosonic Coulomb systems. *Lett. Math. Phys.*, 21:139–149, 1991.

[3] Johann Jakob Balmer. Notiz über die Spectrallinien des Wasserstoffs. *Annalen der Physik*, 261(5):80–87, 1885.

[4] Pedro Balodis. A proof of Scott's correction for matter. *Comm. Math. Phys.*, 249(1):79–132, 2004.

[5] Hans A. Bethe and Edwin E. Salpeter. Quantum mechanics of one- and two-electron atoms. In S. Flügge, editor, *Handbuch der Physik, XXXV*, pages 88–436. Springer, Berlin, 1 edition, 1957.

[6] G. E. Brown and D. G. Ravenhall. On the interaction of two electrons. *Proc. Roy. Soc. London Ser. A.*, 208:552–559, 1951.

[7] Li Chen and Heinz Siedentop. Positivity of $|\mathfrak{p}|^a|\mathfrak{q}|^b + |\mathfrak{q}|^b|\mathfrak{p}|^a$. *J. Funct. Anal.*, 264(12):2817–2824, 2013.

[8] C. G. Darwin. The wave equations of the electron. *Proc. R. Soc. Lond., Ser. A*, 118:654–680, 1928.

[9] J.P. Desclaux. Relativistic Dirac-Fock Expectation Values for Atoms with $Z = 1$ to $Z = 120$. *Atomic Data and Nuclear Data Tables*, 12(4):311–406, 1973.

[10] William Desmond Evans, Peter Perry, and Heinz Siedentop. The spectrum of relativistic one-electron atoms according to Bethe and Salpeter. *Comm. Math. Phys.*, 178(3):733–746, July 1996.

[11] C. Fefferman and L. Seco. Eigenfunctions and eigenvalues of ordinary differential operators. *Adv. Math.*, 95(2):145–305, October 1992.

[12] C. Fefferman and L. Seco. The density of a one-dimensional potential. *Adv. Math.*, 107(2):187–364, September 1994.

[13] C. Fefferman and L. Seco. The eigenvalue sum of a one-dimensional potential. *Adv. Math.*, 108(2):263–335, October 1994.

[14] C. Fefferman and L. Seco. On the Dirac and Schwinger corrections to the ground-state energy of an atom. *Adv. Math.*, 107(1):1–188, August 1994.

[15] C. Fefferman and L. Seco. The density in a three-dimensional radial potential. *Adv. Math.*, 111(1):88–161, March 1995.

[16] C. L. Fefferman and L. A. Seco. An upper bound for the number of electrons in a large ion. *Proc. Nat. Acad. Sci. USA*, 86:3464–3465, 1989.

[17] C. L. Fefferman and L. A. Seco. Asymptotic neutrality of large ions. *Comm. Math. Phys.*, 128:109–130, 1990.

[18] C. L. Fefferman and L. A. Seco. On the energy of a large atom. *Bull. AMS*, 23(2):525–530, October 1990.

[19] Charles L. Fefferman and Luis A. Seco. Aperiodicity of the Hamiltonian flow in the Thomas-Fermi potential. *Revista Mathemática Iberoamericana*, 9(3):409–551, 1993.

[20] E. Fermi. Un metodo statistico per la determinazione di alcune proprietá dell'atomo. *Atti della Reale Accademia Nazionale dei Lincei, Rendiconti, Classe di Scienze Fisiche, Matematiche e Naturali*, 6(12):602–607, 1927.

[21] E. Fermi. Eine statistische Methode zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendung auf die Theorie des periodischen Systems der Elemente. *Z. Phys.*, 48:73–79, 1928.

[22] Rupert L. Frank, Heinz Siedentop, and Simone Warzel. The ground state energy of heavy atoms: Relativistic lowering of the leading energy correction. *Comm. Math. Phys.*, 278(2):549–566, 2008.

[23] Rupert L. Frank, Heinz Siedentop, and Simone Warzel. The energy of heavy atoms according to Brown and Ravenhall: The Scott correction. *Doc. Math.*, 14:463–516, 2009.

[24] P. Gombás. *Die statistische Theorie des Atoms und ihre Anwendungen.* Springer-Verlag, Wien, 1 edition, 1949.

[25] Walter Gordon. Die Energieniveaus des Wasserstoffatoms nach der Diracschen Quantentheorie. *Z. Phys.*, 48:11–14, 1928.

[26] Marcel Griesemer, Roger T. Lewis, and Heinz Siedentop. A minimax principle for eigenvalues in spectral gaps: Dirac operators with Coulomb potential. *Doc. Math.*, 4:275–283, 1999.

[27] Marcel Griesemer and Heinz Siedentop. A minimax principle for the eigenvalues in spectral gaps. *J. London Math. Soc. (2)*, 60(2):490–500, 1999.

[28] Michael Handrek and Heinz Siedentop. The ground state energy of heavy atoms: the leading correction. *Comm. Math. Phys.*, 339(2):589–617, 2015.

[29] Ira W. Herbst. Spectral theory of the operator $(p^2 + m^2)^{1/2} - Ze^2/r$. *Comm. Math. Phys.*, 53:285–294, 1977.

[30] Webster Hughes. *An Atomic Energy Lower Bound that Gives Scott's Correction.* PhD thesis, Princeton, Department of Mathematics, 1986.

[31] Webster Hughes. An atomic lower bound that agrees with Scott's correction. *Adv. in Math.*, 79:213–270, 1990.

[32] V. Ja. Ivrii and I. M. Sigal. Asymptotics of the ground state energies of large Coulomb systems. *Annals of Math.*, 138(2):243–335, 1993.

[33] Wolfgang jun. Pauli. Über den Zusammenhang des Abschlusses der Elektronengruppen im Atom mit der Komplexstruktur der Spektren. *Z. Phys.*, 31:765–783, 1925.

[34] Tosio Kato. On the existence of solutions of the helium wave equation. *Trans. Amer. Math. Soc.*, 70:212–218, 1951.

[35] Tosio Kato. *Perturbation Theory for Linear Operators*, volume 132 of *Grundlehren der mathematischen Wissenschaften.* Springer-Verlag, Berlin, 1 edition, 1966.

[36] A. Kramida, Yu. Ralchenko, J. Reader, and and NIST ASD Team. NIST Atomic Spectra Database (ver. 5.2), [Online]. Available: `http://physics.nist.gov/asd` [2014, November 6]. National Institute of Standards and Technology, Gaithersburg, MD., 2014.

[37] W. Lenz. Über die Anwendbarkeit der statistischen Methode auf Ionengitter. *Z. Phys.*, 77:713–721, 1932.

[38] Elliott H. Lieb and Barry Simon. The Thomas-Fermi theory of atoms, molecules and solids. *Advances in Math.*, 23(1):22–116, 1977.

[39] Paul Mancas, A. M. Klaus Müller, and Heinz Siedentop. The optimal size of the exchange hole and reduction to one-particle Hamiltonians. *Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta)*, 111(1):49–53, February 2004.

[40] Sergey Morozov and David Müller. On the minimax principle for Coulomb-Dirac operators. *Math. Z.*, 280(3-4):733–747, 2015.

[41] David Müller. Minimax principles, Hardy-Dirac inequalities, and operator cores for two and three dimensional Coulomb-Dirac operators. *Doc. Math.*, 21:1151–1169, 2016.

[42] G. Nenciu. Self-adjointness and invariance of the essential spectrum for Dirac operators defined as quadratic forms. *Comm. Math. Phys.*, 48(3):235–247, 1976.

[43] Markus Reiher and Alexander Wolf. *Relativistic Quantum Chemistry: The Fundamental Theory of Molecular Science.* Wiley-VCH, Weinheim, 2009.

[44] E. Schrödinger. Quantisierung als Eigenwertproblem: Dritte Mitteilung. *Annalen der Physik*, 385(13):437–490, 1926.

[45] E. Schrödinger. Quantisierung als Eigenwertproblem (Erste Mitteilung). *Annalen der Physik*, 384(4):361–376, 1926.

[46] E. Schrödinger. Quantisierung als Eigenwertproblem: Zweite Mitteilung. *Annalen der Physik*, 384(6):489–527, 1926.

[47] Julian Schwinger. Thomas-Fermi model: The leading correction. *Phys. Rev. A*, 22(5):1827–1832, 1980.

[48] J. M. C. Scott. The binding energy of the Thomas-Fermi atom. *Phil. Mag.*, 43:859–867, 1952.

[49] Heinz Siedentop and Rudi Weikard. On the leading energy correction for the statistical model of the atom: Interacting case. *Comm. Math. Phys.*, 112:471–490, 1987.

[50] Heinz Siedentop and Rudi Weikard. Upper bound on the ground state energy of atoms that proves Scott's conjecture. *Phys. Lett. A*, 120:341–342, 1987.

[51] Heinz Siedentop and Rudi Weikard. On the leading energy correction of the statistical atom: Lower bound. *Europhysics Letters*, 6:189–192, 1988.

[52] Heinz Siedentop and Rudi Weikard. On the leading correction of the Thomas-Fermi model: Lower bound – with an appendix by A. M. K. Müller. *Invent. Math.*, 97:159–193, 1989.

[53] Heinz Siedentop and Rudi Weikard. A new phase space localization technique with application to the sum of negative eigenvalues of Schrödinger operators. *Annales Scientifiques de l'École Normale Supérieure*, 24(2):215–225, 1991.

[54] Heinz K. H. Siedentop and Rudi Weikard. On the leading energy correction for the statistical model of the atom: Non-interacting case. *Abh. Braunschweig. Wiss. Ges.*, 38:145–158, 1986.

[55] Jan Philip Solovej, Thomas Østergaard Sørensen, and Wolfgang L. Spitzer. The relativistic Scott correction for atoms and molecules. *Commun. Pure Appl. Math.*, 63:39–118, January 2010.

[56] Jan Philip Solovej and Wolfgang L. Spitzer. A new coherent states approach to semiclassics which gives Scott's correction. *Comm. Math. Phys.*, 241(2-3):383–420, 2003.

[57] Arnold Sommerfeld. Zur Quantentheorie der Spektrallinien. *Annalen der Physik*, 356(17):1–94, 1916.

[58] G. Stell. Fluids with long-range forces: Toward a simple analytic theory. In Bruce J. Berne, editor, *Statistical Mechanics*, volume 5 of *Modern Theoretical Chemistry*, pages 47–84. Springer US, 1977.

[59] J. Sucher. Foundations of the relativistic theory of many-electron atoms. *Phys. Rev. A*, 22(2):348–362, August 1980.

[60] L. H. Thomas. The calculation of atomic fields. *Proc. Camb. Phil. Soc.*, 23:542–548, 1927.

[61] C. Tix. Lower bound for the ground state energy of the no-pair Hamiltonian. *Phys. Lett. B*, 405(3-4):293–296, 1997.

[62] C. Tix. Self-adjointness and spectral properties of a pseudo-relativistic Hamiltonian due to Brown and Ravenhall. *Preprint*, mp-arc: 97-441, 1997.

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